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CERTIFICATE OF MAILING
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Germaine Brenkert
Germaine Brenkert
Dated: April 17, 2007

IN THE UNITED STATES PATENT AND TRADEMARK OFFICE

Applicant : Areal Guerra Rogelio
Application No. : 09/744,655
Patent No. : 6,743,336
Issue Date : June 1, 2004
For : COMPOSITION FOR DE-ACIDIFICATION OF CELLULOSE MATERIAL
Examiner : Steve Alvo

**Mail Stop Certificate of Correction Branch
Commissioner for Patents
P.O. Box 1450
Alexandria, Virginia 22313-1450**

REQUEST & PETITION FOR CERTIFICATE OF CORRECTION

Sir:

Upon reviewing the Letters Patent document issued for the above-identified application, typographical errors, were made on the part of the Applicant. The Commissioner is respectfully requested to issue the attached Certificate of Correction with

each copy of the above-identified U.S. Patent.

The errors identified in the specification of the patent are of a clerical nature in that they involve an error in the translation of the PCT application, PCT/ES99/00242 on which the U.S. patent is a section 371 application and thus incorporates its subject matter. Accordingly, no new matter is being added to the patent.

In greater detail, the correction sought for the patent at column 3, lines 43 and 44, changing "[1.8 D]" to --[μ:1.8 D]--, "[0.40 D]" to --[μ:0.40 D]-- and "[1.5 D]" to --[μ:1.5 D]--. Similarly, at column 5, lines 5, 8 and 18 changing "50 and 150 m" to --50 and 150 μm--. The same correction is requested for column 9, lines 15 and 16 of the patent. The symbol "μ" has inadvertently been omitted in each instance.

Support for these corrections can be found in the PCT application which was published as WO 00/08250 at page 6, lines 12-14; page 9, lines 9 and 24 and page 17, lines 14 and 15 of the published PCT application.

Relevant corrected copies of the patent and the underlying PCT application are attached as well as the certificate itself.

Applicant hereby petitions to correct the patent under 37 CFR 1.183, and hereby encloses a check in the amount of \$400 as set forth in 37 CFR 1.17(f).

The required Form PTO-1050 is attached hereto, along with the fee of \$100 under 37 C.F.R. § 1.323. The Commissioner is also hereby authorized to charge Deposit Account No. 14-1431 for any additional fees which may be due.

If there should be any questions, please do not hesitate to contact the undersigned.

Favorable action is respectfully requested.

Dated: April 17, 2007

Respectfully submitted,



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**UNITED STATES PATENT AND TRADEMARK OFFICE
CERTIFICATE OF CORRECTION**Page 1 of 1

PATENT NO. : 6,743,336
APPLICATION NO.: 09/744,655
ISSUE DATE : June 1, 2004
INVENTOR(S) : Areal Guerra Rogelio

It is certified that an error appears or errors appear in the above-identified patent and that said Letters Patent is hereby corrected as shown below:

Column 3, line 43, change "[1.8 D]" to --[μ :1.8 D]--.

Column 3, line 44, change "[0.40 D] and n-propanol [1.5 D]" to --[μ :0.40 D] and n-propanol [μ :1.5 D]--.

Column 5, line 5, change "50 to 150 m" to --50 and 150 μ m--.

Column 5, line 8, change "50 to 150 m" to --50 and 150 μ m--.

Column 5, line 18, change "(50-150-m)" to --(50-150 μ m)--.

Column 9, lines 15 to 16, change "50 and 100 m" to --50 and 100 μ m--.

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This collection of information is required by 37 CFR 1.322, 1.323, and 1.324. The information is required to obtain or retain a benefit by the public which is to file (and by the USPTO to process) an application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 1.0 hour to complete, including gathering, preparing, and submitting the completed application form to the USPTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, P.O. Box 1450, Alexandria, VA 22313-1450. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Attention Certificate of Corrections Branch, Commissioner for Patents, P.O. Box 1450, Alexandria, VA 22313-1450.

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US006743336B1

(12) **United States Patent**
Rogelio

(10) **Patent No.: US 6,743,336 B1**
(45) **Date of Patent: Jun. 1, 2004**

(54) **COMPOSITION FOR DE-ACIDIFICATION
OF CELLULOSE MATERIAL**

(75) **Inventor: Areal Guerra Rogelio, Terrassa (ES)**

(73) **Assignee: Universitat Politecnica de Catalunya,
Terrassa (ES)**

(*) **Notice:** Subject to any disclaimer, the term of this
patent is extended or adjusted under 35
U.S.C. 154(b) by 0 days.

(21) **Appl. No.: 09/744,655**

(22) **PCT Filed: Jul. 29, 1999**

(86) **PCT No.: PCT/ES99/00242**

§ 371 (c)(1),

(2), (4) **Date: Mar. 16, 2001**

(87) **PCT Pub. No.: WO00/08250**

PCT Pub. Date: Feb. 17, 2000

(30) **Foreign Application Priority Data**

Jul. 31, 1998 (ES) 9801737

(51) **Int. Cl.⁷ D21H 17/72; D21H 25/18**

(52) **U.S. Cl. 162/160; 162/183; 162/184;
252/380; 252/384; 422/40; 427/439**

(58) **Field of Search** 162/160, 181.4,
162/181.5, 77, 90, 72; 427/537, 538, 439,
537.5, 702; 422/40

(56) **References Cited**

FOREIGN PATENT DOCUMENTS

CA 2142195 A1 * 8/1996

* cited by examiner

Primary Examiner—Steve Alvo

(74) *Attorney, Agent, or Firm*—Notaro & Michalos P.C.

(57) **ABSTRACT**

The product is presented in the form of a solution and is composed of carbonated magnesium di-n-propylate, n-propanol, and a hydrofluorocarbon (HFC) diluent selected from 1,1,1,2-tetrafluoroethane (HFC 134a) and 1,1,1,2,3,3,3-heptafluoropropane (HFC 227). The product may be obtained by a procedure which comprises preparing a solution of carbonated magnesium di-n-propylate in n-propanol and diluting said solution by addition of the HFC diluent. The product is suitable for de-acidifying cellulose-type material and preserving objects based on cellulose-type material.

5 Claims, No Drawings

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radiation, thus reducing the potential for ozone destruction. On the other hand, the presence of hydrogen means that the compound is more reactive, such that it tends to decompose more easily before reaching the stratosphere. The rate of decomposition of HCFCs and HFCs is higher than that of the CFCs, whose lifetime is quoted at being between 60 and 100 years.

The object of the present invention is to find a new product for the non-aqueous de-acidification of cellulose-type materials, thus providing an addition to the arsenal of means available for combating acidification of cellulose-type materials.

Therefore, an object of this invention consists of a product, in the form of a solution, for the non-aqueous de-acidification of cellulose-type materials which comprises carbonated magnesium di-n-propylate, n-propanol and an HFC diluent.

An additional object of this invention consists of a procedure for production of said product for the de-acidification of cellulose-type material.

Another additional object of this invention consists of a method for de-acidification of cellulose-type material which comprises use of the aforementioned product.

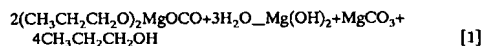
DETAILED DESCRIPTION OF THE INVENTION

The present invention provides a product for de-acidification of cellulose-type material, hereinafter denominated the product of the invention, characterized because it is presented in the form of a solution and is comprised of:

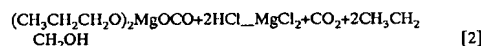
carbonated magnesium di-n-propylate,
n-propanol, and

an HFC diluent selected from 1,1,1,2-tetrafluoroethane (HFC 134a) y 1,1,1,2,3,3,3-heptafluoropropane (HFC 227).

Carbonated magnesium di-n-propylate is a white solid, with the formula $(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_2\text{MgOCO}$, soluble in anhydrous n-propanol and in medium-polarity solvents, such as HFC 227 and HFC 134a, whose polarities are 0.8 Debyes (D). The meaning of the term "organic solvents of medium polarity" in this description includes solvents with a dipole moment (μ) less than water (1.8 D), for example, toluene (0.40 D) and n-propanol (0.3 D). Carbonated magnesium di-n-propylate has a dipole moment of 0.8 D and so, in general, it is soluble in any proportion in the HFC diluent used for producing the product of the invention. The dipole moment of this diluent is approximately 0.9 D. Carbonated magnesium di-n-propylate, on coming into contact with moist air, reacts to give magnesium carbonate and magnesium hydroxide, and slowly releases n-propanol according to the reaction [1]:



Carbonated magnesium di-n-propylate reacts vigorously with mineral acids releasing carbon dioxide and n-propanol, forming soluble magnesium salts as indicated by reaction [2]:



As a result of the high solubility of carbonated magnesium di-n-propylate in polar solvents, characterized by low surface tension and viscosity values, it can be dispersed deeply through the pores in the paper, reaching all points of cellulose-type material, and neutralizing the acids present.

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The excess reagent slowly decomposes into magnesium carbonate hydroxide, a stable compound of the formula $(\text{MgCO}_3)_4\text{Mg}(\text{OH})_2 \cdot 5\text{H}_2\text{O}$, which it deposited among the paper fibres to act as a alkaline reservoir protecting against acidic atmospheric contaminants and acids released in the paper during ageing. The trials carried out on papers treated and submitted to accelerated ageing have shown that treatment with the product of the invention [see Example 3] stabilizes the properties of the mechanical resistance of the paper, manifesting itself as a stabilization in the degree of whiteness.

Carbonated magnesium di-n-propylate can be obtained from magnesium di-n-propylate by a procedure that comprises the stages of:

reacting a suspension of magnesium di-n-propylate in n-propanol with gaseous anhydrous carbon dioxide, until a solution of carbonated magnesium di-n-propylate is obtained; and

separating said solution of carbonated magnesium di-n-propylate in n-propanol from the residual products, for example by decantation.

Reaction of magnesium di-n-propylate with anhydrous carbon dioxide is an exothermic reaction, reaching temperatures of up to 45° C. and the initial solid compound insoluble in n-propanol [magnesium di-n-propylate] is transformed into a soluble form consisting of carbonated magnesium di-n-propylate. The reaction is taken to have reached its conclusion when the temperature drops to room temperature. Next, the dark solid insoluble particles are allowed to sediment out on the bottom of the recipient and to give a clear and transparent solution. The resulting solution is collected by conventional techniques, for example, by decantation or, preferably, by suction under vacuum, and transferred to recipients suitable for loading, dilution or dosing. The carbonated magnesium di-n-propylate obtained is purified, for example, by evaporation of part of the solvent (typically 20–30%) under vacuum.

The concentration of carbonated magnesium di-n-propylate in the alcoholic solution lies between 30 and 70% (P/P), preferably between 45 and 50% (P/P) of carbonated magnesium di-n-propylate, the rest consisting of n-propanol. It can be adjusted to the desired concentration by conventional methods, for example, by dilution with n-propanol or by elimination of excess solvent.

Magnesium alkoxides can be obtained using known methods for example, *Metal Alkoxides*, by Bradley, D. C., Mehrotra, R. C. and Gaur, D. P., Academic Press, London (1978), and the work of Thoms, H., Epple, M., Viebrock, H. and Reller, A., *J. Mater. Chem.* 5(4)589, (1995), where the synthesis of different magnesium alkoxides from alcohols of up to four carbon atoms is described. Although various magnesium alkoxides are known, the literature only describes carbonated magnesium alkoxides derived from methanol (methoxymagnesium methylcarbonate) and ethanol (ethoxymagnesium ethylcarbonate) and the carbonate of methoxy and butoxy polyethylene glycol [WO 90/03466].

The suspension of magnesium di-n-propylate in n-propanol can be prepared by different procedures. One of them (Procedure A) comprises reacting magnesium metal with anhydrous n-propanol, in the presence of iodine, at the temperature corresponding to the boiling point of the mixture. Another procedure (Procedure B) comprises reacting magnesium metal with anhydrous n-propanol in the presence of iodine at reflux temperature and the addition of toluene to form an azeotrope with n-propanol. The magnesium metal used in either Procedure A or B may in the form of a strip, in which case, it requires a suitable preparation (see Example 1.2).

$[\mu: 1.80 \text{ D}]$

$[\mu: 0.40 \text{ D}]$

$[\mu: 1.80 \text{ D}]$

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Alternatively, the suspension of magnesium di-n-propylate in n-propanol can be prepared by a procedure (Procedure C) which does not require the use of a strip of magnesium but rather magnesium in powder form, with a granulometric distribution between 50 and 150 μ m. This procedure C therefore comprises of: (i) reacting magnesium in powder form, with a granulometric distribution between 50 and 150 μ m, with anhydrous n-propanol in the presence of iodine, which acts as a catalyst. The mixture is gently heated until hydrogen begins to be released. From this moment on, as the reaction is strongly exothermic, the next step (ii) consists of cooling the reaction mixture to the temperature corresponding to the boiling point, with a view to controlling the reaction rate with gentle boiling until hydrogen is no longer given off and the last remaining particles of magnesium have disappeared. In this fashion a suspension of magnesium di-n-propylate in n-propanol is obtained.

The use of magnesium in the form of powder with the indicated granulometric distribution (50–150 μ m) means that the reaction of magnesium with n-propanol in the presence of iodine is exothermic, and so the reaction medium should be cooled instead of additional energy being provided. This also allows the reaction time to be reduced [typically, the total reaction time for production of magnesium di-n-propylate is 4–5 hours].

Carbonated magnesium di-n-propylate can be used in the production of a product, in the form of a solution, suitable for de-acidification of cellulose-type material along with n-propanol, and a diluent selected from HFC 134a and HFC 227.

The meaning of "cellulose-type material" as used in this description refers to a material totally or partially composed of cellulose fibres, including paper of all classes, tissues and fabrics which contain cellulose fibres of vegetal origin, for example, those produced from wood, cotton, flax, jute, hemp and other plants. Examples of such cellulose-type materials include books, documents, maps, works of art, articles elaborated with said materials, clothing, flags, etc.

For use as a reagent for de-acidification of cellulose-type material a solution of carbonated magnesium di-n-propylate and n-propanol is produced, in HFC diluent, at a concentration lying between 30% and 70% (W/V) for application by machine and of 3.5% to 4.5% (W/V) in said HFC diluent for application by sprays. In general, said solution is of light chestnut colour and viscous. To reduce as much as possible the unwanted effects of the alcohol on the components of the paper, it is useful to concentrate the resulting solution as much as possible while maintaining a suitable fluidity for dosing.

The concentrated solution of carbonated magnesium di-n-propylate is diluted to the desired concentration with a chemically inert and non-toxic diluent which allows the de-acidifying reagent to be carried inside the cellulose-type material. An HFC selected from HFC 134a and HFC 227 can be used as diluent. HFC 227 is preferable. HFC 227 has a boiling point of -17.3°C . at normal pressure (101.3 kPa), a liquid density of 1.417 g/cm^3 at 20°C . (399.3 kPa). The surface tensions are 9.31 mN/m (at 0°C .), 6.96 mN/m (at 20°C .) and 4.8 mN/m (at 40°C .) and its dipole moment is $0.2\pm 0.14\text{ D}$. HFC 227 has been marketed since 1991 as a substitute for R12 and R114 in sectors where these chemicals have been used as coolants. The company SOLVAY brought this product onto the market at the beginning of 1996 as, in September 1995, the European Commission for Pharmaceutical Products in Brussels (CPMP) established that HFC 227 was suitable for pharmaceutical inhalers.

Dilution of the concentrated solution of carbonated magnesium di-n-propylate is carried out with the chosen HFC,

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preferably HFC 227, in pressurized containers, up to de-acidification reagent concentrations [carbonated magnesium di-n-propylate] lying between 1% and 10% (W/V), preferably between 1% and 10% (W/V) and up to concentrations of n-propanol less than 10% (V/V). In a particular and preferred embodiment of the invention, the product of the invention contains between 3.8 and 4.5% (W/V) of carbonated magnesium di-n-propylate, between 2 and 3% (V/V) of n-propanol, the rest of the mixture consisting of the HFC diluent chosen from HFC 227 and HFC 134a, and the product of the invention of said formulation is especially suitable for use with spray systems.

Additionally and optionally, the product of the invention may contain an inert gas, for example, nitrogen, with a view to achieving additional pressure and propulsion.

The resulting diluted solutions of carbonated magnesium di-n-propylate may be applied by conventional methods, for example, by direct spray onto the cellulose-type material. This method of applying the de-acidification product does not require prior desiccation, under vacuum, of the cellulose-type material, as the distribution and impregnation attained using the spray is very uniform and does not lead to the accumulation of any type of deposit or residue on the cellulose-type material to be treated. In general, it is advisable to work in a fume cupboard and use means of personal protection to avoid inhaling the spray.

The product of de-acidification product of the cellulose-type material can also be carried out by means of dissolving in HFC to a known concentration, for the bulk de-acidification of books and documents, using the equipment and method described in the Spanish patent application P9600016 filed by the same applicant. The apparatus described is formed of a treatment chamber, which serves for the drying stages under vacuum prior to impregnation and recovery of solvent by evaporation-condensation.

Therefore, the invention also provides a method for de-acidification of cellulose-type material, which comprises the application, of a quantity sufficient of the product of the invention for de-acidifying the cellulose-type material to be treated. The product of the invention may be applied to the cellulose-type material to be treated by means of a bulk de-acidification system or by spray.

The product of the invention can be obtained through a procedure that comprises:

- preparing a solution of carbonated magnesium di-n-propylate in n-propanol; and
- diluting said solution by addition of an HFC diluent selected from among HFC 134a and HFC 227.

In a particular embodiment, the concentration of carbonated magnesium di-n-propylate in said alcoholic solution lies between 30% and 70% (W/V).

Additionally and optionally, the product of the invention may contain an inert gas, for example, nitrogen.

The following examples serve as an illustration of the present invention and should not be considered as limiting the scope thereof.

EXAMPLE 1

Preparation of Carbonated Magnesium di-n-propylate

1.1 Dehydration of n-propanol

To dehydrate n-propanol a procedure such as the one described by A. I. Vogel, in "Practical Organic Chemistry", 3rd Ed. Longmans, London, 1961, pag. 168, is used, duly modified for the case of n-propanol.

Thus it can be affirmed that the product is soluble at any proportion. The carbonated magnesium di-n-propylate is soluble in HFC 134a in analogue proportions.

EXAMPLE 2

Preparation of Carbonated Magnesium di-n-propylate

2.1 Preparation of Magnesium di-n-propylate (Procedure C)

In a 5-liter round-bottomed flask, 3.750 ml of anhydrous n-propanol are placed (3 kg, 50 mols), prepared according to the procedure described in Example 1.1. Next, 146 g (6 mols) of magnesium metal are added in the form of a powder with a granulometric distribution lying between 50 and 100 μ m, along with 7.5 g of iodine as a catalyst. Next the mixture is heated gently until hydrogen begins to be given off, and from then on, as the reaction is strongly exothermic, the reaction medium is cooled with a view to controlling the rate of reaction at a gentle boiling for six hours until hydrogen is not longer released and the last particles of magnesium have disappeared. A suspension of magnesium di-n-propylate, a light grey-coloured solid, is obtained in n-propanol. The mixture is allowed to cool before proceeding to the next step in the reaction. 770–800 g of product are obtained, with yields between 90–92%.

2.2 Preparation of Carbonated Magnesium di-n-propylate

A current of carbon dioxide, completely anhydrous after passing through two drying towers full of anhydrite, is passed through the suspension of magnesium di-n-propylate in n-propanol. The reaction is exothermic, reaching temperatures of 45° C. The solid starting product [magnesium di-n-propylate] is transformed into a soluble form consisting of carbonated magnesium di-n-propylate. The reaction is over after 4–6 hours. When the temperature drops to room temperature the product is allowed to sediment out for 24–48 hours until the solid dark insoluble particles are lying at the bottom of the flask, and the solution appears clear and transparent. This solution may be collected by decantation or even better transferred by suction under vacuum, to recipients appropriate for loading, dilution or dosing. The magnesium content in this solution, measured by complexometric titration, is greater than 5%, which represents 40% as carbonated magnesium di-n-propylate.

The product is purified by total evaporation of n-propanol under vacuum, and the Mg content analysed by complexometric titration, and the CO₂ content is determined by decomposition of a sample with concentrated phosphoric acid and collection of CO₂ in a series of towers containing a known excess of barium hydroxide. The results obtained coincide with these mentioned in Example 1.5.

EXAMPLE 3

Efficacy Assays

In order to check the efficacy of a product for the de-acidification of the cellulose-type material provided by the invention some assays have been carried out to determine the absorption of said product on a cellulose-type material to assay, along with some assays to determine the mechanical characteristics of the cellulose-type material treated.

Parallel to this, by way of comparison, a commercial paper de-acidification product [Bookkeeper] of high efficiency has been assayed and the results compared in each case.

3.1 Absorption Assays

The absorption of the product for de-acidification constitutes an indication of the alkaline reserve created in the cellulose-type material. This reservoir may play an important role in combating the degradation of cellulose by acid hydrolysis and, therefore, is going to contribute to the better preservation of the cellulose material.

In the assays carried out to check the efficacy of the product provided by the invention the cellulose-type material used was paper in different stages of ageing (without ageing and submitted to accelerated ageing).

Briefly, the assay carried out consisted of applying the product for de-acidifying the paper to the sheets of paper, either to one side or to both sides, and then determining the alkaline reserve created in the paper. Assays have been affected in different conditions of ageing of the paper. The results obtained are shown in Tables 1–3.

3.1.A. Without Ageing

The results obtained at zero time, in other words, without submitting the paper to an accelerated ageing process are shown in Table 1.

TABLE 1

Efficacy assay (Without ageing of the paper)						
Sample	Initial weight (g)	Dry weight (g)	Humidity (%)	HCl	NaOH	Alkaline reserve (mol/kg)
Bookkeeper 1 side	1.017	0.948	6.78	2.565	2.39	0.184
Bookkeeper 2 sides	1.006	0.923	8.18	2.565	2.25	0.341
Invention 1 side	1.012	0.910	10.9	2.565	2.01	0.609
Invention 2 sides	1.006	0.905	10.1	2.565	1.5	1.176

Bookkeeper: Commercial product comprising micronised magnesium oxide, a humectant and a freon.

Invention: Solution of carbonated magnesium di-n-propylate and n-propanol in an HFC diluent selected from HFC 134a and HFC 227, at 4%.

HCl: No. of HCl equivalents.

NaOH: No. of NaOH equivalents.

As can be seen, the alkaline reserve created by the product of the invention is very much better (a little greater than three times better) than that created using Bookkeeper.

3.1.B. Accelerated Ageing (5 Years)

Additional assays were carried out submitting the paper to an accelerated ageing process, consisting of keeping the paper in a chamber at a temperature of 90° C. and a relative humidity of 50%. Under these conditions, 1 hour of treatment of the paper is equivalent to an ageing of 7.5 days. Next, the product is applied to the aged paper with the cellulose-type material to be de-acidified. In Table 2 the results obtained after submitting the paper to a 10-day treatment are shown. This period corresponds to an ageing of the paper of 5 years.

TABLE 2

Efficacy assay (Accelerated ageing of the paper: 5 years)						
Sample	Initial weight (g)	Dry weight (g)	Humidity (%)	HCl	NaOH	Alkaline reserve (mol/kg)
Bookkeeper 1 side	1.015	0.962	5.57	2.565	2.40	0.171

PCT ORGANIZACION MUNDIAL DE LA PROPIEDAD INTELECTUAL
 Oficina Internacional
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 EN MATERIA DE PATENTES (PCT)**

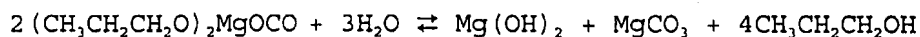


(51) Clasificación Internacional de Patentes ⁷ : D21C	A2	(11) Número de publicación internacional: WO 00/08250 (43) Fecha de publicación internacional: 17 de Febrero de 2000 (17.02.00)						
(21) Solicitud internacional: PCT/ES99/00242 (22) Fecha de la presentación internacional: 29 de Julio de 1999 (29.07.99) (30) Datos relativos a la prioridad: <table style="width: 100%;"> <tr> <td style="width: 30%;">P 9801733</td> <td style="width: 30%;">31 de Julio de 1998 (31.07.98)</td> <td style="width: 40%;">ES</td> </tr> <tr> <td>P 9801737</td> <td>31 de Julio de 1998 (31.07.98)</td> <td>ES</td> </tr> </table> (71) Solicitante (para todos los Estados designados salvo US): UNIVERSITAT POLITÈCNICA DE CATALUNYA [ES/ES]; Colom, 11, E-08222 Terrassa (ES). (72) Inventor; e (75) Inventor/solicitante (sólo US): AREAL GUERRA, Rogelio [ES/ES]; Colom, 11, E-08222 Terrassa (ES). (74) Mandatario: CARPINTERO LOPEZ, Francisco; Herrero & Asociados, S.L., Alcalá, 35, E-28014 Madrid (ES).		P 9801733	31 de Julio de 1998 (31.07.98)	ES	P 9801737	31 de Julio de 1998 (31.07.98)	ES	(51) Estados designados: AE, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, CA, CH, CN, CU, CZ, DE, DK, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, SL, TJ, TM, TR, TT, UA, UG, US, UZ, VN, YU, ZA, ZW, Patente ARIPO (GH, GM, KE, LS, MW, SD, SL, SZ, UG, ZW), Patente euroasiática (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), Patente europea (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), Patente OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GW, ML, MR, NE, SN, TD, TG). Publicada <i>Sin informe de búsqueda internacional, será publicada nuevamente cuando se reciba dicho informe.</i>
P 9801733	31 de Julio de 1998 (31.07.98)	ES						
P 9801737	31 de Julio de 1998 (31.07.98)	ES						
(54) Title: PRODUCT FOR DESACIDIFICATION OF CELLULOSE MATERIAL, PRODUCTION AND UTILIZATION THEREOF (54) Título: PRODUCTO PARA LA DESACIDIFICACION DE MATERIAL CELULOSICO, SU OBTENCION Y EMPLEO (57) Abstract The product is in the form of a solution and is comprised of carbonated magnesium di-n-propylate, n-propanol and a hydrofluorocarbonated diluent (HFC) selected between 1,1,1,2-tetrafluoroethane (HFC 134a) and 1,1,1,2,3,3,3-heptafluoropropane (HFC 227). The product can be obtained through a process which comprises the preparation of a solution of di-n-propylate of magnesium carbonate into n-propanol and diluting said solution by addition of the diluent HFC. The product is appropriate for desacidification of cellulose material and preservation of objects based on cellulose material. (57) Resumen El producto se presenta en forma de una disolución y está compuesto por di-n-propilato de magnesio carbonatado, n-propanol, y un diluyente hidrofluorocarbonado (HFC) seleccionado entre 1,1,1,2-tetrafluoroetano (HFC 134a) y 1,1,1,2,3,3,3-heptafluoro-propano (HFC 227). El producto puede obtenerse mediante un procedimiento que comprende preparar una solución de di-n-propilato de magnesio carbonatado en n-propanol y diluir dicha solución por adición del diluyente HFC. El producto es adecuado para desacidificar material celulósico y preservar objetos a base de material celulósico.								



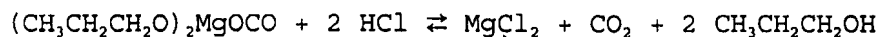
- n-propanol, y
- un diluyente HFC seleccionado entre 1,1,1,2-tetrafluoro-etano (HFC 134a) y 1,1,1,2,3,3,3-heptafluoropropano (HFC 227).

5 El di-n-propilato de magnesio carbonatado es un sólido blanco, de fórmula $(\text{CH}_3\text{CH}_2\text{CH}_2\text{O})_2\text{MgOCO}$, soluble en n-propanol anhidro y en disolventes orgánicos de polaridad media, tales como el HFC 227 y el HFC 134a, cuyas polaridades son de 0,8 Debyes (D). En el sentido
10 utilizado en esta descripción, el término "disolventes orgánicos de polaridad media" incluye los disolventes con un momento dipolar (μ) menor al del agua [μ : 1,8 D], por
12 ejemplo, el tolueno [μ : 0,40 D] y el n-propanol [μ : 1,5
13 D]. El di-n-propilato de magnesio carbonatado tiene un
14 momento dipolar de 0,8 D por lo que, en general, se
15 disuelve en cualquier proporción en el diluyente HFC
utilizado en la elaboración del producto de la invención,
cuyo momento dipolar típico es de 0,9 D aproximadamente.
El di-n-propilato de magnesio carbonatado, en contacto
20 con el aire húmedo reacciona dando carbonato de magnesio
e hidróxido de magnesio, y liberando lentamente n-
propanol según se muestra en la reacción [1]:



25 [1]

El di-n-propilato de magnesio carbonatado reacciona
enérgicamente con los ácidos minerales liberando dióxido
de carbono y n-propanol, y formándose sales magnésicas
30 solubles según se muestra en la reacción [2]:



[2]

35 Debido a la elevada solubilidad del di-n-propilato
de magnesio carbonatado en disolventes polares,
caracterizados por valores bajos de tensión superficial



magnesio metal utilizado en cualquiera de los Procedimientos A y B puede encontrarse en forma de cinta, en cuyo caso, necesita una preparación adecuada (véase el Ejemplo 1.2).

5 Alternativamente, la suspensión de di-n-propilato de magnesio en n-propanol puede prepararse por un procedimiento (Procedimiento C) que no requiere el empleo de cinta de magnesio sino de magnesio en forma de polvo, con una granulometría de 50 a 150 μm . Este Procedimiento C comprende, por tanto, (i) hacer reaccionar magnesio en forma de polvo con una granulometría comprendida entre 50 y 150 μm con n-propanol anhidro en presencia de yodo, que actúa como catalizador, calentando suavemente hasta que comienza el desprendimiento de hidrógeno, y, a partir de ese momento, como la reacción es fuertemente exotérmica, (ii) refrigerar la mezcla de reacción hasta la temperatura de ebullición, con el fin de controlar la velocidad de la reacción a ebullición suave hasta que cesa el desprendimiento de hidrógeno y desaparecen las últimas partículas de magnesio, obteniéndose de esta manera una suspensión de di-n-propilato de magnesio en n-propanol.

15 El uso de magnesio en forma de polvo con la granulometría indicada (50-150 μm) hace que la reacción del magnesio con el n-propanol en presencia de yodo sea exotérmica, con lo que se debe enfriar el medio de reacción en lugar de aportar energía externa adicional, y permite, además, acortar el tiempo de reacción [típicamente, el tiempo total de reacción para la obtención del di-n-propilato de magnesio es de 4-5 horas].

25 El di-n-propilato de magnesio carbonatado puede utilizarse en la elaboración de un producto, en forma de disolución, adecuado para la desacidificación de material celulósico junto con n-propanol, y un diluyente seleccionado entre el HFC 134a y el HFC 227.

35 En el sentido utilizado en esta descripción, el



proporciones análogas.

EJEMPLO 2

Preparación de di-n-propilato de magnesio carbonatado

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2.1 Preparación de di-n-propilato de magnesio

(Procedimiento C)

En un matraz de fondo redondo de 5 l de capacidad, provisto de un refrigerante de reflujo protegido con un tubo de cloruro cálcico anhidro, se colocan 3.750 ml de n-propanol anhidro (3 kg, 50 moles) preparado según el procedimiento descrito en el Ejemplo 1.1, y, a continuación, se añaden 146 g (6 moles) de magnesio metal en polvo con una granulometría comprendida entre 50 y 100 μm y 7,5 g de yodo como catalizador. A continuación, la mezcla de reacción se calienta suavemente hasta que se inicia el desprendimiento de hidrógeno y, a partir de ese momento, como la reacción es fuertemente exotérmica, se refrigera el medio de reacción con el fin de controlar la velocidad de la reacción a ebullición suave, durante 6 horas, hasta que cesa el desprendimiento de hidrógeno y desaparecen las últimas partículas de magnesio. Se obtiene una suspensión en n-propanol del di-n-propilato de magnesio, sólido de color gris claro. Se deja enfriar para proceder al siguiente paso de la reacción. Se obtiene una cantidad de producto de 770-800 g, con rendimientos entre 90-92%.

2.2 Preparación de di-n-propilato de magnesio carbonatado

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A través de la suspensión de di-n-propilato de magnesio en n-propanol obtenida en el Ejemplo 2.1, se hace pasar una corriente de dióxido de carbono completamente anhidro después de pasar por dos torres de secado rellenas de anhídrita. La reacción es exotérmica, alcanzándose temperaturas de hasta 45°C. El compuesto sólido de partida [di-n-propilato de magnesio] va

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